INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, VOL. 41, 311–325 (1992)

Vector Coupling Coefficients for Calculations of Transition-Metal Atoms and Ions by the SCF Coupling Operator Method

B. N. PLAKHUTIN AND G. M. ZHIDOMIROV
Institute of Catalysis, Novosibirsk, 630090, USSR
A. V. ARBUZNIKOV
Department of Natural Sciences, State University, Novosibirsk, 630090, USSR

Abstract

We derived the necessary conditions to which the vector coupling coefficients (VCC) $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$, describing atomic L,S-multiplets of the configurations d^N ($1 \leqslant N \leqslant 9$), should satisfy. Special attention is paid to the states of non-Roothaan type for which VCC depend on the choice of degenerate d-orbitals basis set determined within the accuracy up to an orthogonal transformation u. It is shown that for such states the direct sum of matrices $\|a_{mn}^{(u)}\|$ and $\|b_{mn}^{(u)}\|$ must be the non-symmetric matrix. Obtained VCC were used for the ab initio calculations (basis set (14*s*9*p*5*d*)/[8*s*4*p*2*d*] from [15]) on first-row transition atoms (from Sc to Cu) to compare to similar calculations [16], in which the Peterson's VCC have been used, and with calculations [15] carried out by the atomic SCF program [4] as well.

1. Introduction

The problem of calculation of transition-metal atoms and ions by the restricted Hartree–Fock method was discussed in the literature for a long period of time. A fundamental contribution to the solution of this problem has been made by Slater, Racah, Condon, and others [1, 2]. The essential result of their investigations was the representation of the energy of a separate state (L,S-multiplet [1]) in terms of the Slater–Condon parameters F^k and G^k. Specifically, for most of the multiplets ^{2s+1}L, arising from the configurations d^N ($1 \leqslant N \leqslant 9$), the energy $E_s^L = E(^{2s+1}L)$ can be expressed as follows [1, 2]:

$$E_s^L = E' + c^{(0)}F^0 + c^{(2)}F^2 + c^{(4)}F^4, \tag{1}$$

where $\Sigma_k c^{(k)}F^k$ is the energy of electronic repulsion within the open d-shell; E' is the rest of the multiplet energy that is described by the same expression for all the states of the configuration; $F^k = F^k(d,d)$ are the Slater–Condon parameters; and $c^{(k)}$ are numerical constants that characterize the electronic configuration and the state under consideration. The main difficulty for the theory was connected to the derivation of similar expressions for the multiplet energies in cases of more complicated configurations such as $d^{N_1}p^{N_2}$ [1, 2].

CCC 0020-7608/92/020311-15$04.00

The first specialized quantum-chemical program for the ab initio calculations on atoms by the expansion method appeared in [3]. An analogous but more perfect program [4] was widely used later for the systematic calculations on atoms of the periodic table [5]. The computational scheme of the programs [3, 4] is based on the Roothaan–Hartree–Fock equations for atoms [3]. The principal peculiarity of the theory [3] consists in the fact that an arbitrary collection of the partially occupied atomic n, l shells (all with different l) is described as one open electronic shell (i.e., all the partially occupied atomic orbitals are described by the single open-shell coupling operator F^0). Specifically, the atoms with the electronic configurations d^N ($1 \leqslant N \leqslant 9$) are described in such a way.

Such peculiarity of the algorithm [3], taking explicitly into account the high symmetry of an atom, considerably simplifies the Hartree–Fock calculations of the transition atoms. However, this technique cannot be used within the standard "molecular" programs utilizing the restricted Hartree–Fock method (RHF) for the open-shell systems [6–10]. In contrast to the theory [3], in the RHF method, it is necessary to describe every atomic degenerate d-orbital by its own Fock operator (with subsequent eliminating of off-diagonal Lagrange multipliers by constructing the general SCF coupling operator R [7–9] or by directly solving a system of coupled equations containing these multipliers. [10]).

In the course of such calculations, the main difficulty consists of the correct description of the spin and spatial symmetry of an atom in its definite ("non-Roothaan" [11, 12]) spectroscopic states in terms of the vector coupling coefficients. This difficulty has not yet been overcome [13, 14]. Moreover, Domingo and Burgos [14] have voiced the supposition that the problem of calculation on the transition-metal atoms within the framework of the coupling operator method [9] cannot be solved at all.

In this paper, we present a detailed analysis of the problem of calculations on the transition-metal atoms within the framework of the RHF method [7–10]. We derive the necessary conditions that the vector coupling coefficients (VCC) $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$, which describe in the RHF method the electronic configuration and the state, should satisfy. The obtained VCC were used for the ab initio calculations (basis set $(14s9p5d)/[8s4p2d]$ from [15]) on the first-row transition atoms (from Sc to Cu) to compare with similar calculations [16], in which the Peterson's VCC have been used, and with calculations [15] carried out by the atomic SCF program [4] as well.

2. Equations Determining VCC for the Configurations d^N of Atoms

In the RHF method, the energy functional for the state of a system with the electronic configuration γ^N (γ is a symmetry of degenerate open-shell MOs) can be represented as follows [6, 9, 11]:

$$E_{state} = E' + f^2 \sum_m \sum_n (2a_{mn}^{(u)} J_{mn} - b_{mn}^{(u)} K_{mn}), \tag{2}$$

where

$$E' = 2\sum_k H_{kk} + \sum_k \sum_l (2J_{kl} - K_{kl}) + 2f\left\{\sum_m H_{mm} + \sum_k \sum_m (2J_{km} - K_{km})\right\}. \tag{3}$$

Here $f = N/2n_\gamma$ is the open-shell occupation number; m and n are the indices for the open-shell orbitals, and k and l, for the closed-shell orbitals; and $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$ are numerical constants characterizing the state and configuration under consideration, being also called the vector coupling coefficients (VCC). For all the atomic states arising from the configurations p^N ($1 \leqslant N \leqslant 5$), these coefficients do not depend on indices m and n, i.e., $a_{mn} = a$, $b_{mn} = b$ [6]. In the molecules of cubic or tetragonal symmetry with electronic configuration t^N ($2 \leqslant N \leqslant 4$) or e^2, the coefficients $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$ also depend on the choice of the basis of the open-shell degenerate MOs [11, 12], which are determined within the accuracy up to a unitary transformation u.

Thus, to calculate a transition-metal atom by the RHF method using the existing open-shell SCF programs (such as MONSTERGAUSS, POLYATOM, etc.), it is necessary to determine the coefficients $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$ (or only a and b for the Roothaan-type states [6]). These coefficients were first proposed by Guest and Saunders in [17]; however, the analysis in [13] showed those coefficients not to be quite correct. The coefficients from [17] correspond not to the L,S-multiplet (i.e., electronic term), but to the S-multiplet, i.e., to the set of states arising from the referent electronic configuration and corresponding to the same value of spin number S (see Discussion below).

The general approach to the calculation of the coefficients $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$ is known to be as follows [6, 9]: (i) Many-electron wave functions $\Psi_{sM_s}^{LM_L}$ corresponding to the given values of quantum numbers L, M_L, s, and M_s are constructed. (ii) Average values of the energy $\langle \Psi_{sM_s}^{LM_L} | \hat{H} | \Psi_{sM_s}^{LM_L} \rangle$ are calculated in terms of integrals H_{mm}, J_{mn}, and K_{mn}. (iii) The average energy of the state

$$E_s^L = \frac{1}{2s+1} \frac{1}{2L+1} \sum_{M_s} \sum_{M_L} \langle \Psi_{sM_s}^{LM_L} | \hat{H} | \Psi_{sM_s}^{LM_L} \rangle \tag{4}$$

is found. The latter is presented in the form of Eq. (2) from which the coefficients a_{mn} and b_{mn} are determined (here, indices m and n are the numbers of the degenerate d-orbitals). Since the real AO basis set is usually used in routine RHF programs, we shall suppose, therefore, that the d-orbitals are given in the following form*:

$$\sigma = d_{z^2}, \quad \pi = d_{xz}, \quad \pi' = d_{yz}, \quad \delta = d_{x^2-y^2}, \quad \delta' = d_{xy}. \tag{5}$$

The scheme, described above for determining the coefficients a_{mn} and b_{mn} [6, 9], does not lead directly to the energy functional in the form of Eq. (2) in the case of configuration d^N, and that is an essential peculiarity that makes differences in states with open d-shell from those arising, e.g., from the configuration p^N. In the expression for E_s^L, besides the terms from Eq. (2), there arises an additional term that consists of the combination of four-indexed integrals $\langle mm' \mid nn' \rangle$. For instance, one can obtain the expression for the energy of the state ^3F arising

*In the iterative SCF process, the degenerate atomic d-orbitals are determined in a random manner that is within the accuracy up to an orthogonal transformation. Therefore, below, we should propose that the d-orbitals to be transformed **at each iteration** into basis set (5) by the corresponding transformation denoted by the symbol u^0.

from the configuration d^2 in the form of

$$E(^3F,d^2) = \text{the right side of Eq. (2)} + \sum_m \sum_{m'} \sum_n \sum_{n'} a_{mm'nn'}\langle mm' \,|\, nn'\rangle, \quad (6)$$

the latter term in Eq. (6) not being identically equal to zero.

Similar complications have occurred in [18] when calculating coefficients a_{mn} and b_{mn} for diatomic molecules in their excited states and in [19] in the calculations of the molecules of symmetry D_{4h} with the electronic configuration $e_g^1 e_u^1$ as well. In the atomic case under consideration, one can eliminate the denoted complication as follows:

It is well known [20] that any four-indexed integral with atomic d-orbitals can be expressed in terms of the Slater–Condon parameters:

$$\begin{aligned}
&\langle\sigma\delta \,|\, \pi'\pi'\rangle = -\langle\sigma\delta' \,|\, \pi\pi'\rangle = -\langle\sigma\delta \,|\, \pi\pi\rangle = 2\sqrt{3}B,\\
&\langle\pi\delta \,|\, \pi'\delta'\rangle = -\langle\pi\delta' \,|\, \pi'\delta\rangle = 3B,\\
&\langle\sigma\pi \,|\, \pi'\delta'\rangle = -\langle\sigma\pi' \,|\, \pi'\delta\rangle = \langle\sigma\pi' \,|\, \pi\delta'\rangle = \langle\sigma\pi \,|\, \pi\delta\rangle = \sqrt{3}B, \qquad (7)
\end{aligned}$$

where $B = (9F^2 - 5F^4)/441$ is the Racah parameter [1] and all the other four-indexed integrals of this type are equal to zero.

Using the identities (7) and the analogous relationships that couple two-indexed integrals ($J_{mn} = \langle mm \,|\, nn\rangle$, $K_{mn} = \langle mn \,|\, mn\rangle$) and the Slater–Condon parameters [20]:

$$\begin{aligned}
J_{mm} &= F^0 + (36F^2 + 36F^4)/441, \qquad (m = \sigma, \pi, \pi', \delta, \delta'),\\
J_{\sigma\pi} &= J_{\sigma\pi'} = F^0 + (18F^2 - 24F^4)/441,\\
J_{\sigma\delta} &= J_{\sigma\delta'} = F^0 + (-36F^2 + 6F^4)/441,\\
J_{\pi\pi'} &= J_{\pi\delta} = J_{\pi\delta'} = J_{\pi'\delta} = J_{\pi'\delta'} = F^0 + (-18F^2 - 4F^4)/441,\\
J_{\delta\delta'} &= F^0 + (36F^2 - 34F^4)/441;\\
K_{\sigma\pi} &= K_{\sigma\pi'} = (9F^2 + 30F^4)/441,\\
K_{\sigma\delta} &= K_{\sigma\delta'} = (36F^2 + 15F^4)/441,\\
K_{\pi\pi'} &= K_{\pi\delta} = K_{\pi\delta'} = K_{\pi'\delta} = K_{\pi'\delta'} = (27F^2 + 20F^4)/441,\\
K_{\delta\delta'} &= 35F^4/441, \qquad (8)
\end{aligned}$$

one can replace all the four-indexed integrals in Eq. (6) by the identical combinations of integrals (8) and, thus, express the ^3F state energy (6) in the form of Eq. (2).

Evidently, such a procedure [of representation E_s^L in the form Eq. (2)] can be carried out for any state arising from the configuration d^N. Moreover, there is no need to use explicit expressions for four-indexed integrals (7) for this purpose. As a matter of fact, it is sufficient to level the right sides of Eqs. (1) and (2):

$$c^{(0)}F^{(0)} + c^{(2)}F^2 + c^{(4)}F^4 = f^2 \sum_m \sum_n (2a_{mn}^{(u)} J_{mn} - b_{mn}^{(u)} K_{mn}) \qquad (9)$$

and to determine the unknown coefficients $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$ in terms of the known values of $c^{(0)}$, $c^{(2)}$, and $c^{(4)}$.

From the substitution of values of integrals J_{mn} and K_{mn} from Eqs. (8) into Eq. (9) and leveling separately the coefficients multiplied by F^0, F^2, and F^4 both on the left and on the right sides of Eq. (9), we obtain three equations for determining 50 ($5 \times 5 \times 2$) unknown quantities:

$$\sum_{j=1}^{50} \lambda_{ij} x_j = c^{(2(i-1))}/f^2, \qquad i = 1,2,3; \tag{10}$$

where x_j are unknowns $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$ ($x_1 = a_{\sigma\sigma}, x_2 = a_{\sigma\pi}, \ldots, x_5 = a_{\sigma\delta'}, x_6 = a_{\pi\sigma}, \ldots, x_{25} = a_{\delta'\delta'}, x_{26} = b_{\sigma\sigma}, \ldots, x_{50} = b_{\delta'\delta'}$); and λ_{ij} are corresponding coefficients attached to the unknown quantities and defined in Eqs. (8).

It is evident that Eqs. (10) can be satisfied with the different sets of coefficients $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$. However, not all these sets are equivalent from the physical point of view. Dealing with the problem of the calculation of VCC for the states arising from the configuration d^N, we meet with an additional complication that did not occur in the similar calculations of VCC for other types of the open shells [9,12–14]. The gist of this problem can be explained as follows:

3. Degeneracy of d-Orbitals

In accordance with the terminology from [11–13], all the states arising from the degenerate open electronic shell γ^N are divided into the "Roothaan's" and "non-Roothaan's" states. The former ones are described only by two VCC, i.e., $a_{mn} = a$ and $b_{mn} = b$ [6]. The values of these coefficients for the Roothaan states arising from the configuration d^N can be derived from Eq. (9):

$$-630f^2b/441 = c^{(2)} = c^{(4)} \tag{11a}$$

$$f^2(50a - 5b) = c^{(0)} = N(N-1)/2 \tag{11b}$$

(additional equation is $c^{(0)} = N(N-1)/2$, which is correct for all the states of the configuration d^N following from the condition of normalization for the two-particle density [13]). Thus, all the Roothaan states arising from the configuration d^N are characterized by the equality $c^{(2)} = c^{(4)}$.

The non-Roothaan states arising from the configuration γ^N of the tetragonal and cubic symmetry systems investigated before [11–13] are described by the symmetric matrices $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$ with the elements depending on the choice of the basis of degenerate orbitals of symmetry γ. Particularly, these matrices can be presented in a more simple form [12, 21]:

$$b_{mn}^{(u^0)} = b, \qquad a_{mn}^{(u^0)} = \delta_{mn}a' + (1 - \delta_{mn})a'' \tag{12}$$

if the definite choice of basis set corresponding to the "standard" assignment of irreducible representation $\gamma = \gamma^0$ is used [22].

The non-Roothaan states occur also in the transition atoms with the electronic configuration d^N. All the states, the energy of which is described by the Eq. (1) with $c^{(2)} \neq c^{(4)}$, are the non-Roothaan ones. In accordance with Eqs. (9)

and (11), such states cannot be described only by two coupling coefficients a and b; for these states, it is necessary to use the matrices a_{mn} and b_{mn}. As these matrices are given in the basis set of the degenerate orbitals, so their elements must depend on the choice of the basis set of d-orbitals [12, 13] (or, in other words, on the choice of orthogonal transformation matrix u, to an accuracy with which the d-orbitals are defined).

It is easy to understand that for the considered non-Roothaan states arising from the configuration d^N the unknown vcc $a_{mn}^{(u^0)}$ and $b_{mn}^{(u^0)}$ cannot be derived in the form of Eq. (12). [In this case, the designations $a_{mn}^{(u^0)}$ and $b_{mn}^{(u^0)}$ mean that coupling coefficients correspond to the basis set of d-orbitals in the form of Eq. (5); see also the footnote to Eq. (5)]. From the substitution of the Eqs. (8) and (12) into Eq. (9), we obtain

$$c^{(2)} = c^{(4)} = f^2\{360(a' - a'') - 630 \times b\}/441,$$

i.e., in case of atoms with the configuration d^N, the coupling coefficients given in the form of Eq. (12) correspond to the state of the Roothaan type.

In the course of calculation of the vcc for different systems with the degenerate open-shell γ^N in [9, 12–14], the problem related to one-electron energy levels of the open-shell $\{\varepsilon_m\} = \{\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_{n_\gamma}\}$, where n_γ is the dimension of irreducible representation γ, was not analyzed. It was tacitly assumed that in case of the configuration γ^N the vcc calculated by the scheme [6, 9] lead automatically to the degeneration of one-electron energies $\{\varepsilon_m\}$. Nevertheless, this problem needs special discussion.

One-electron energies $\{\varepsilon_m\}$ in the framework of the open-shell Hartree–Fock method [6–9] are the eigenvalues of the general coupling operator R:

$$R\phi_m = \phi_m\varepsilon_m. \tag{13}$$

Using the general expression for R derived by Hirao (see Eq. (3.8) in [8]), we obtain

$$\begin{aligned}\varepsilon_m &= \langle\phi_m|R|\phi_m\rangle = \langle\phi_m|F_m|\phi_m\rangle \\ &= f_m\{H_{mm} + \sum_k (2J_{km} - K_{km}) + \sum_n f_n(2a_{mn}^{(u)}J_{mn} - b_{mn}^{(u)}K_{mn})\},\end{aligned} \tag{14}$$

where F_m is the Fock operator for orbital ϕ_m.

In the definition, in case of the orbitals being transformed by the degenerate irreducible representation γ, it should be

$$\varepsilon_1 = \varepsilon_2 = \ldots = \varepsilon_{n_\gamma}. \tag{15}$$

Because the occupation numbers f_m as well as the core integrals H_{mm} and the sums $\Sigma_k(2J_{km} - K_{km})$ have the same values for all the degenerate orbitals $\{\phi_m\}$ [6],

$$\sum_n (2a_{mn}^{(u)}J_{mn} - b_{mn}^{(u)}K_{mn}) = \sum_n (2a_{\underline{m}n}^{(u)}J_{\underline{m}n} - b_{\underline{m}n}^{(u)}K_{\underline{m}n}), \tag{16}$$

where $\underline{m} > m$ and $n = 1, 2, \ldots, n_\gamma$ (for d-orbitals $n = \sigma, \pi, \pi', \delta, \delta'$).

Our analysis showed that the VCC $a_{mn}^{(u^0)}$ and $b_{mn}^{(u^0)}$ calculated in [12,13] for the states of the molecular systems with the configurations t^N and e^N do satisfy (identically) Eqs. (15) and (16). On the other hand, the coupling coefficients for the non-Roothaan states of the configuration d^N calculated by Eq. (9) do not satisfy relationships (16) automatically. As a matter of fact, the last ones should be considered to be the additional equations [together with Eqs. (9) and (10)] for the determination of the coefficients $a_{mn}^{(u^0)}(^{2s+1}L, d^N)$ and $b_{mn}^{(u^0)}(^{2s+1}L, d^N)$.

From the substitution of values of integrals from Eq. (8) into Eq. (16) and carrying out the transformations similar to above [see Eqs. (9) and (10) and respective text], we obtain the $12 = 3 \times (n_d - 1)$ linear uniform equations:

$$\sum_{j=1}^{50} \lambda_{ij} x_j = 0, \qquad i = 4,5,\ldots,15. \tag{17}$$

Thus, keeping in mind Eqs. (10), one has **15** equations for determination of **50** unknown quantities. The computer analysis of these equations[†] provided us with the following conclusion. In case of the non-Roothaan states [i.e., with $c^{(2)} \neq c^{(4)}$], Eqs. (10) and (17) are consistent if and only if the matrix $\|a_{mn}^{(u^0)}\|$ and/or matrix $\|b_{mn}^{(u^0)}\|$ is nonsymmetric.[‡]

In other words, if one introduces the matrix $\|Z_{mn}^{(u^0)}\|$, which is the direct sum of matrices $\|a_{mn}^{(u^0)}\|$ and $\|b_{mn}^{(u^0)}\|$,

$$\|Z_{mn}^{(u^0)}\| = \|a_{mn}^{(u^0)}\| \oplus \|b_{mn}^{(u^0)}\|, \tag{18}$$

the necessary condition of consistency of Eqs. (10) and (17), from one side, and the inequality $c^{(2)} \neq c^{(4)}$, from the other side, can be presented as follows:

$$\|Z_{mn}^{(u^0)}\| \neq \|Z_{mn}^{(u^0)}\|^T, \tag{19}$$

where the superscript ^{T} denotes the transposition.

Thus, the non-Roothaan states arising from the configuration d^N $(2 \leqslant N \leqslant 8)$ are described in the RHF method by the nonsymmetric matrix $\|Z_{mn}^{(u^0)}\|$. To a certain extent, this result is unusual. For all the open electronic shells investigated before (see [9,11–14,18]), it was always possible to present the corresponding matrix in the symmetric form. In this connection, it should be pointed out that the nonsymmetricity of the VCC matrix $\|Z_{mn}^{(u^0)}\|$ does not lead to the nonsymmetricity (non-Hermiticity) of the Fock matrices [see Eq. (14)].

[†]Because of the rationality of the coefficients λ_{ij} from Eqs. (10) and (17), the last ones can be solved in integers, allowing elimination of the truncation errors at computer calculations.

[‡]If both matrices $\|a_{mn}^{(u^0)}\|$ and $\|b_{mn}^{(u^0)}\|$ are symmetric and their elements satisfy Eqs. (17), it may be shown that

$$\sum_{j=1}^{50} \lambda_{2,j} x_j = \sum_{j=1}^{50} \lambda_{3,j} x_j$$

with consequence $c^{(2)} = c^{(4)}$ [see Eq. (10)]. The latter implies that only the Roothaan-type states can be described by the symmetric matrices $\|a_{mn}^{(u^0)}\|$ and $\|b_{mn}^{(u^0)}\|$.

The general solution of Eqs. (10) and (17) contains **50 − 15 = 35** arbitrary parameters. To obtain the coefficients $a_{mn}^{(u^0)}$ and $b_{mn}^{(u^0)}$ in a more convenient form, we introduced the additional relationships that do not contradict Eqs. (9), (16), and (19):

$$b_{mn}^{(u^0)} = \beta, \qquad a_{mm}^{(u^0)} = a'. \tag{20}$$

These relationships reduce the number of the unknowns $a_{mn}^{(u^0)}$ and $b_{mn}^{(u^0)}$ to **22** and simultaneously reduce the number of linearly independent Eqs. (17) to **8**. Moreover, the coefficients $a_{mn}^{(u^0)}$ were constrained by the conditions

$$\begin{aligned} &a_{\sigma\pi} = a_{\sigma\pi'}, \qquad a_{\sigma\delta} = a_{\sigma\delta'}, \qquad a_{\pi\pi'} = a_{\pi\delta} = a_{\pi\delta'} \\ &a_{\delta\pi} = a_{\delta\pi'}, \qquad a_{\delta'\pi} = a_{\delta'\pi'}, \qquad a_{\pi'\pi} = a_{\pi'\delta} = a_{\pi'\delta'}, \end{aligned} \tag{21}$$

which follow in a natural way from Eqs. (9) and (16). [Unknown quantities $a_{\sigma\pi}$ and $a_{\sigma\pi'}$, $a_{\sigma\delta}$ and $a_{\sigma\delta'}, \ldots$, enter Eqs. (9) and (16) with equal coefficients; therefore, additional relationships (21) do not change the number of linearly independent equations but reduce the number of the unknowns to **14**].

Taking into account Eqs. (20) and (21), finally we have **11** Eqs. (10) and (17) to determine **14** unknowns. The solution of these equations gives the following expressions for the coefficients $a_{mn}^{(u^0)}$ ($^{2s+1}L, d^N$):

$$\begin{aligned} a' &= (2c^{(0)} + 35c^{(2)} + 63c^{(4)})/100f^2 + 3\beta/2, \\ a_{\delta'\sigma} &= (-4c^{(0)} - 140c^{(2)} + 189c^{(4)})/100f^2 + \beta/2 + 3\omega_0, \\ a_{\delta'\pi} &= 3(4c^{(0)} + 35c^{(2)} - 84c^{(4)})/200f^2 - 3\beta/4 - 2\omega_0; \end{aligned} \tag{22}$$

$$\begin{aligned} a_{\sigma\pi} &= (a_{\delta'\pi} + 2\omega_0)/3, \\ a_{\sigma\delta} &= a_{\pi\pi'} = a_{\pi'\pi} = (3a_{\delta'\sigma} + 4a_{\delta'\pi} - \omega_0)/6, \\ a_{\delta\sigma} &= a_{\delta'\sigma} + 3\omega - 3\omega_0, \\ a_{\delta\pi} &= a_{\delta'\pi} - 2\omega + 2\omega_0, \\ a_{\pi\sigma} &= a_{\pi'\sigma} = -(a_{\delta'\sigma} - 3\omega_0)/2, \\ a_{\delta\delta'} &= \omega, \\ a_{\delta'\delta} &= \omega_0 \end{aligned} \tag{23}$$

where β, ω, and ω_0 are arbitrary numbers.

Thus, in case of atoms with the open d-shell, the matrices of coupling coefficients $a_{mn}^{(u^0)}$ and $b_{mn}^{(u^0)}$, characterizing within the framework of the coupling operator method the state and configuration, have only three independent values [$a_{mm} = a'$, $a_{\delta'\sigma}$, and $a_{\delta'\pi}$; see Eqs. (22)] that correspond to the number of independent coefficients ($c^{(0)}$, $c^{(2)}$, and $c^{(4)}$) in Eq. (1).[§]

[§]In the atomic theory [3] for transition elements instead of coefficients $c^{(0)}$, $c^{(2)}$, and $c^{(4)}$, the coupling coefficients K_{220}, K_{222}, and K_{224} are used [23]. Since the latter are linearly connected with the coefficients $c^{(i)}$, one can express the vcc $a_{mn}^{(u^0)}$ (22) in terms of K_{22i} coefficients as well.

The obtained relationships [Eqs. (20)–(23)] allow us to present VCC $a_{mn}^{(u^0)}$ in different ways, changing values of arbitrary parameters β, ω, and ω_0. In particular, in case of the Roothaan states [i.e., with $c^{(2)} = c^{(4)}$], the coupling coefficients (20)–(23) can be expressed in the form of Eq. (12) if we put $a'' = \omega_0 = \omega = a_{\delta'\sigma}$. Furthermore, if we put the arbitrary parameter β to be equal $\beta = -7c^{(2)}/10f^2 = b$, we can obtain VCC in the standard Roothaan form $a_{mn}^{(u^0)} = a$, $b_{mn}^{(u^0)} = b$ [6] satisfying Eq. (11).

It should be pointed out that coefficients $a_{mn}^{(u^0)}$ given in the general form [Eq. (20)–(23)] correspond to the definite choice of the degenerate d-orbitals basis set [Eq. (5)]. When one uses any other basis set, the coefficients $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$ must be changed correspondingly. The independence of VCC on the choice of the basis set for the Roothaan states arises only because of the above constraints on free parameters β, ω, and ω_0.

Table I presents as an example the general form of the matrix $\|a_{mn}^{(u^0)}\|$ containing arbitrary parameters β, ω, and ω_0 for the state ^4P of the configuration d^3.

Table II contains the coefficients $a_{mn}^{(u^0)} = a$ and $b_{mn}^{(u^0)} = b$ for all the Roothaan-type states arising from the configurations d^N ($1 \leq N \leq 9$).

In Table III we present the nonsymmetric matrices $a_{mn}^{(u^0)}$ for the several non-Roothaan states (lowest in energy in the respective electronic configurations d^N), which were obtained from Eqs. (20)–(23) with $\beta = \omega = \omega_0 = 0$. A general form of these matrices with nonzero arbitrary parameters β, ω, and ω_0 can be easily obtained, as is shown in Table I.

It is necessary to point out that in our calculations discussed below we used different sets of arbitrary parameters β, ω, and ω_0 for checking the presented theory. The calculated values of the energy and other physical characteristics indeed do not depend on the values of these parameters. This result is not a trivial

TABLE I. A general form of the matrix $a_{mn}^{(u^0)}$ for the state ^4P of the configuration d^3 satisfying Eqs. (9), (16), and (19)–(23). (β, ω, and ω_0 are the arbitrary numbers; $b_{mn}^{(u^0)} = \beta$).

	σ	π	π'	δ	δ'
σ	$\frac{-5}{3} + \frac{3\beta}{2}$	$\frac{40}{18} - \frac{\beta}{4}$	$\frac{40}{18} - \frac{\beta}{4}$	$\frac{5}{18} - \frac{\beta}{4}$	$\frac{5}{18} - \frac{\beta}{4}$
π	$\frac{75}{18} - \frac{\beta}{4}$	$\frac{-5}{3} + \frac{3\beta}{2}$	$\frac{5}{18} - \frac{\beta}{4}$	$\frac{5}{18} - \frac{\beta}{4}$	$\frac{5}{18} - \frac{\beta}{4}$
π'	$\frac{75}{18} - \frac{\beta}{4}$	$\frac{5}{18} - \frac{\beta}{4}$	$\frac{-5}{3} + \frac{3\beta}{2}$	$\frac{5}{18} - \frac{\beta}{4}$	$\frac{5}{18} - \frac{\beta}{4}$
δ	$\frac{-150}{18} + \frac{\beta}{2} + 3\omega$	$\frac{120}{18} - \frac{3\beta}{4} - 2\omega$	$\frac{120}{18} - \frac{3\beta}{4} - 2\omega$	$\frac{-5}{3} + \frac{3\beta}{2}$	ω
δ'	$\frac{-150}{18} + \frac{\beta}{2} + 3\omega_0$	$\frac{120}{18} - \frac{3\beta}{4} - 2\omega_0$	$\frac{120}{18} - \frac{3\beta}{4} - 2\omega_0$	ω_0	$\frac{-5}{3} + \frac{3\beta}{2}$

Note: Coefficients $a_{mn}^{(u^0)}$ for any other state arising from the configuration d^N (N = 1–9) differ from those presented in Table I only by the first term, which does not contain the arbitrary parameters β, ω, and ω_0 (see Tables II and III).

TABLE II. The vector coupling coefficients $a_{mn}^{(u^0)} = a$ and $b_{mn}^{(u^0)} = b$ for the Roothaan atomic states arising from the configurations d^N.

Configuration, state	a[a]	b[a]	$c^{(2)} = c^{(4)}$,[b] [1]
$d^1, {}^2D$	0	0	0
$d^2, {}^1S$	0	−5	126/441
$d^4, {}^5D$	15/16	15/8	−189/441
$d^5, {}^6S$	1	2	−315/441
$d^6, {}^5D$	35/36	25/18	−315/441
$d^8, {}^1S$	15/16	10/16	−252/441
$d^9, {}^2D$	80/81	80/81	−504/441

[a]These values of a and b correspond to the following values of arbitrary parameters: $\beta = -7c^{(2)}/10f^2 = b$ and $\omega = \omega_0 = a$ [see Eqs. (20)–(23) and respective text, and Eqs. (11) as well].

[b]Values of $c^{(2)}$ and $c^{(4)}$ presented in Tables II and III differ from those presented in Slater's monograph ($c^{(2)}_{\text{Slater}}$, $c^{(4)}_{\text{Slater}}$) [1], as the latter correspond to the following expression of the state energy

$$E_s^L = E_{av} + c^{(2)}_{\text{Slater}} F^2 + c^{(4)}_{\text{Slater}} F^4,$$

where E_{av} is the average energy of the configuration d^N:

$$E_{av} = E' + N(N-1) \times \left\{ \frac{1}{2} F^0 - \frac{7}{441}(F^2 + F^4) \right\}$$

and E' is defined in Eqs. (1)–(3). Thus, $c^{(0)} = N(N-1)/2$, and $c^{(2)} = c^{(2)}_{\text{Slater}} - 7N(N-1)/441$, and $c^{(4)} = c^{(4)}_{\text{Slater}} - 7N(N-1)/441$.

TABLE III. The vector coupling coefficients $a_{mn}^{(u^0)}$ for the lowest non-Roothaan states, arising from the configurations d^N ($b_{mn}^{(u^0)} = \beta$).

	σ	π	π'	δ	δ'
State ${}^3F$ (d^2); [$c^{(2)} = -72/441$, $c^{(4)} = -9/441$]					
σ	−5/4	0	0	15/8	15/8
π	−15/8	−5/4	15/8	15/8	15/8
π'	−15/8	15/8	−5/4	15/8	15/8
δ	30/8	0	0	−5/4	0
δ'	30/8	0	0	0	−5/4
State ${}^4F$ (d^3); [$c^{(2)} = -135/441$, $c^{(4)} = -72/441$]					
σ	−5/3	5/6	5/6	10/6	10/6
π	0	−5/3	10/6	10/6	10/6
π'	0	10/6	−5/3	10/6	10/6
δ	0	15/6	15/6	−5/3	0
δ'	0	15/6	15/6	0	−5/3
State ${}^4P$ (d^3); [$c^{(2)} = 0$, $c^{(4)} = -147/441$]					
σ	−5/3	40/18	40/18	5/18	5/18
π	75/18	−5/3	5/18	5/18	5/18

TABLE III. (*Continued*)

	σ	π	π'	δ	δ'
π'	75/18	5/18	−5/3	5/18	5/18
δ	−150/18	120/18	120/18	−5/3	0
δ'	−150/18	120/18	120/18	0	−5/3
	State ^2G (d^3); $[c^{(2)} = -99/441, c^{(4)} = 13/441]$				
σ	0	5/54	5/54	85/54	85/54
π	−75/54	0	85/54	85/54	85/54
π'	−75/54	85/54	0	85/54	85/54
δ	150/54	15/54	15/54	0	0
δ'	150/54	15/54	15/54	0	0
	States ^2H, ^2P (d^3); $[c^{(2)} = -54/441, c^{(4)} = -12/441]$				
σ	0	5/9	5/9	10/9	10/9
π	0	0	10/9	10/9	10/9
π'	0	10/9	0	10/9	10/9
δ	0	15/9	15/9	0	0
δ'	0	15/9	15/9	0	0
	State ^2F (d^3); $[c^{(2)} = 81/441, c^{(4)} = -87/441]$				
σ	0	35/18	35/18	−5/18	−5/18
π	75/18	0	−5/18	−5/18	−5/18
π'	75/18	−5/18	0	−5/18	−5/18
δ	−150/18	105/18	105/18	0	0
δ'	−150/18	105/18	105/18	0	0
	State ^4F (d^7); $[c^{(2)} = -387/441, c^{(4)} = -324/441]$				
σ	−5/7	115/98	115/98	130/98	130/98
π	100/98	−5/7	130/98	130/98	130/98
π'	100/98	130/98	−5/7	130/98	130/98
δ	−200/98	345/98	345/98	−5/7	0
δ'	−200/98	345/98	345/98	0	−5/7
	State ^3F (d^8); $[c^{(2)} = -450/441, c^{(4)} = -387/441]$				
σ	−35/64	150/128	150/128	165/128	165/128
π	135/128	−35/64	165/128	165/128	165/128
π'	135/128	165/128	−35/64	165/128	165/128
δ	−270/128	450/128	450/128	−35/64	0
δ'	−270/128	450/128	450/128	0	−35/64

Arbitrary values β, ω, and ω_0 are put to be equal to zero for all the states (see Table I for comparison).

one. The latter means that two proposed equations [Eqs. (9) and (16)] are necessary and *enough* for calculating the VCC for the configurations d^N. But in accordance with [24], it is not a general case. In analogous calculations of the VCC for other atomic configurations, one needs additional equations having no analogy with Eqs. (9) and (16).

Using the VCC from Tables II and III, we carried out calculations on the first-row transition atoms (from Sc to Cu) with the Gaussian basis set (14*s*9*p*5*d*)/[8*s*4*p*2*d*] from [15] in order to compare them with similar calculations [16] in which the Peterson's VCC were used and with calculations [15] carried out by the atomic SCF program [4] as well. We used the MONSTERGAUSS-81 program [25] that utilizes the RHF method for the open-shell systems [10].

The necessary modifications of the RHF procedure were made to provide an adequate description of the non-Roothaan states. These included (i) the possibility of dealing with the nonsymmetric matrices $\|a_{mn}^{(u^0)}\|$ and $\|b_{mn}^{(u^0)}\|$ being realized and (ii) the *d*-orbitals basis set transformation procedure into the form of Eq. (5) being added to.

The results of our calculations (total atomic energies) are compared with similar data from [15, 16] in Table IV. To add to this, we carried out calculations on several excited states of the vanadium atom (configuration $\ldots d^3$) that were not considered in [15, 16] to provide possible independent comparison between the two methods of calculation on the transition-metal atoms. The respective results are given in Table IV as well.

4. Discussion

Comparison of our results with the data from [15], obtained by the atomic program, points to their coincidence, as it should (see Table IV; the differences in

TABLE IV. Total energy (a.u.) (basis set (14*s*9*p*5*d*)/[8*s*4*p*2*d*] from [15]).

Atom; state; configuration	RHF calculation using the "molecular" program MONSTERGAUSS		Calculation [15] using the atomic program [4]
	Present work[a]	[16][b]	
Sc; ^2D; (d^1)	−759.705047	−759.705047	−759.7050
Ti; ^3F; (d^2)	−848.367900	(−848.349942)	−848.3685
V; ^4F; (d^3)	−942.837196	(−942.817440)	−942.8372
$E_s = 3/2$	−942.817440[c]	—	—
^4P;	−942.771401	—	—
^2G;	−942.770986	—	—
^2H, ^2P	−942.749087	—	—
^2F;	−942.683500	—	—
Cr; ^5D; (d^4)	−1043.249620	−1043.249620	−1043.2497
Mn; ^6S; (d^5)	−1149.787155	−1149.787155	−1149.7872
Fe; ^5D; (d^6)	−1262.350361	−1262.350361	−1262.3504
Co; ^4F; (d^7)	−1381.289383	(−1381.263774)	−1381.2895
Ni; ^3F; (d^8)	−1506.720591	(−1506.693632)	−1506.7206
Cu; ^2D; (d^9)	−1638.786455	−1638.786455	−1638.7867
^2S; $(d^{10}s^1)$	−1638.801243	−1638.801243	−1638.8015

Contraction of the basis set [15]: CONTRACTION 3 for Sc to Fe and CONTRACTION 1 for Co to Cu.

[a]Calculations carried out with the VCC from Tables II and III.

[b]Calculations carried out with the VCC obtained by Peterson (see [16, pp. 67–69]).

[c]The average multiplet energy [see Eq. (25) and the corresponding text].

total energy at about 0.0001–0.0006 a.u. for Ti, Cr, Co, and Cu atoms can be presumably ascribed to using the different convergence criteria). On the other hand, our data (and the data from [15] as well) are only partially consistent with the results of calculation from [16]. Although in cases of Sc, Cr, Mn, Fe, and Cu atoms, there is the coincidence of the results; for Ti, V, Co, and Ni atoms, the essential discrepancies are observed (see Table IV).

The analysis of the reasons for these discrepancies reveals that they take place only for those atoms, the lowest state of which is of the non-Roothaan type [i.e., with $c^{(2)} \neq c^{(4)}$; see Table III]. The corresponding states ^3F (Ti, Ni) and ^4F (V, Co) were calculated in [16] using the coupling coefficients $A_{mn} = 2f^2a_{mn}$ and $B_{mn} = f^2b_{mn}$, obtained by Peterson in the symmetric matrix form (see [16, pp. 67–69]):

$$A_{mn} = \delta_{mn}A' + (1 - \delta_{mn})A''$$
$$B_{mn} = \delta_{mn}B' + (1 - \delta_{mn})B''. \tag{24a}$$

As shown in this work (see Section 3), the non-Roothaan states arising from the configurations d^N cannot be described by the symmetric matrices $\|a_{mn}\|$ and $\|b_{mn}\|$ (or $\|A_{mn}\|$ and $\|B_{mn}\|$). Our numerical check showed that the VCC from [16] describing the ^3F (d^2, d^8) and ^4F (d^3, d^7) states do not satisfy Eqs. (9) and (10) and therefore cannot be considered as characteristic values of the spectroscopic states under consideration.

Taking into account the results from Section 3, one can conclude that the coefficients [Eq. (24a)] correspond in reality to the energy functional of the Roothaan type [6] and, hence, can be presented in the form

$$A_{mn} = A'', \qquad B_{mn} = B'' \tag{24b}$$

[as $(A' - B') = (A'' - B'')$; see [16, pp. 67–69]). Comparison of the coefficients [Eq. (24b)] with those obtained in [17] shows their identity. On the other hand, the vector coupling coefficients derived by Guest and Saunders [17] are shown in [13] to correspond not to the separate spectroscopic state energy $E_s^L = E(^{2s+1}L)$ but to the average multiplet energy E_s [13, 21]:

$$E_s = \sum_L (2L + 1) \times E_s^L \Big/ \sum_L (2L + 1). \tag{25}$$

(The coupling coefficients from [17] are reproduced by the general formulas determining the values of $a(E_s)$ and $b(E_s)$; see [13, Eqs. (13)]). Therefore, the Peterson's coefficients (24a) also correspond to the average multiplet energy E_s (with $s = s_{max}$ for the given electronic configuration). To check this conclusion, we calculated the average multiplet energy $E_{s=3/2}$ for the vanadium atom (configuration d^3, $s = 3/2$) using the VCC from [17]. The comparison of the energy $E_{s=3/2}$ with the energy of the vanadium atom from [16] points to their equality (see the values underlined in Table IV). Consequently, the energies of Ti, V, Co, and Ni atoms obtained in [16] do correspond to the average multiplet energy E_s [Eq. (25)] and therefore cannot be considered as the energies of the lowest spectroscopic states.

To conclude, it should be noted that Eqs. (9) and (16) obtained in the present paper for evaluation of the vector coupling coefficients for the configurations d^N

are not valid for all the possible states. The proposed theory does not describe the multiple (double) states such as $^2D_1, ^2D_2$ of the configuration d^3 [1, 2], the energy of which cannot be expressed in the form of Eq. (1).

The theory discussed above can also be extended to the several electronic states arising from the configurations $d^N s^1$ and $d^{N_1} p^{N_2}$. Such generalizations with some actual applications will be presented elsewhere [24].

5. Some Additional Remarks

After this paper was completed, the authors became acquainted with a recent paper [26], several results from which are in sharp contradiction with the above results.

Particularly, in [26], such states as $^2D_1$ (d^3), $^1S_1$ (d^4), $^2D_1$ (d^5) and other **multiple (double) states are considered as the Roothaan-type ones** and the VCC a and b for them are presented (see Table III in [26]).[‖]

It is well known [1, 2] that the energy of the multiple states cannot be represented by Eq. (1) and, consequently, as has been shown above, cannot be expressed in the form of Roothaan's energy functional [i.e., in the form of Eq. (2) with $a_{mn}^{(u)} = a$ and $b_{mn}^{(u)} = b$] [6], since there is a mutual relationship between the coefficients $c^{(0)}$, $c^{(2)}$, and $c^{(4)}$ in Eq. (1), from one side, and the coefficients a and b in Eq. (2), from the other side [see Eqs. (11)]. This means that the above-mentioned multiple states cannot be correctly calculated within the framework of the Roothaan open-shell SCF theory [6].

To calculate the energy of such states as $^2D_1$ and $^2D_2$ (d^3), one has to solve additionally the secular problem in the basis set of two $\Psi(^2D)$ functions with the matrix elements, presented in [1, 2]. (For details, see [1, Sec. 21.1]). The same problem holds if one uses the general SCF coupling operator method [8] instead of the atomic Hartree–Fock theory [1–3].

Concerning the values of the coefficients a and b, presented in [26] for the state ^2D (d^3) and other multiple ones (including those for the systems of the icosahedral symmetry), it should be pointed that they do not correspond to the true energy of a state (which is an eigenvalue of the secular problem). These coefficients correspond to the one of the diagonal matrix element for which $c^{(2)} = c^{(4)}$ (see Table A21a-1 in [1]).

A complete list of the Roothaan-type states arising from the configurations d^N ($1 \leqslant N \leqslant 9$) is presented in Table II.

6. Acknowledgments

The authors would like to thank Prof. P.V. Schastnev and Dr. V. G. Zakrzewski for the valuable discussions of this paper. Also, the authors wish to thank Prof. M. M. Mestechkin for kindly sending a preprint of his article.

[‖]We used the Slater notations for the multiple (double) states. In Table III of [26], such states are situated in the following s,u lines: ($^2D_1$:d^3, 1/2, 1/2), ($^1S_1$:d^4, 0, 0), ($^2D_1$:d^5, 1/2, 1/2), ($^1S_1$:d^6, 0, 0), ($^2D_1$:d^7, 1/2, 1/2).

Bibliography

[1] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vols. I and II.
[2] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1959).
[3] C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press, New York, 1963), Vol. 2, pp. 47–95.
[4] B. Roos, C. Salez, A. Veillard, and E. Clementi, *A General Program for Calculation of Atomic SCF Orbitals by the Expansion Method.* Technical Report RJ-518, IBM Research (1968).
[5] E. Clementi and C. Roetti, Atomic Data Nucl. Data Tables **14**, 177 (1974). A. D. McLean, *Non-relativistic Analytical Atomic SCF Wavefunctions and Radial Expectation Values.* IBM Research Reports RJ-2295 (1978) and RJ-2296 (1978).
[6] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).
[7] G. G. Djadjusha and V. A. Kuprievich, Teoret. Eksperim. Khim. **1**, 406, (1965) (in Russian).
[8] K. Hirao and H. Nakatsuji, J. Chem. Phys. **59**, 1457 (1973). K. Hirao, *Ibid.* **60**, 3215 (1974).
[9] R. Carbo and J. M. Riera, *A General SCF Theory* Lecture Notes in Chemistry, Vol. 5. (Springer-Verlag, Berlin, 1978).
[10] J. Hinze and E. Yutsever, J. Chem. Phys. **70**, 3188 (1979).
[11] B. N. Plakhutin and G. M. Zhidomirov, J. Struct. Chem. **27**, 179 (1986) (translated from Russian by Plenum).
[12] B. N. Plakhutin, G.T. Klimko, M. M. Mestechkin, and G. M. Zhidomirov, Theoret. Exp. Chem. **23**, 123 (1987) (translated from Russian by Plenum).
[13] G.T. Klimko, M. M. Mestechkin, B. N. Plakhutin, et al., Int. J. Quantum Chem. **37**, 35 (1990).
[14] LI. Domingo and J. I. Burgos, in *Proceedings of International Workshop on Quantum Chemistry, Girona, Spain, 1988;* Stud. Phys. Theoret. Chem. **62**, 103 (1989).
[15] A. J. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).
[16] R. Poirier, R. Kari, and I. G. Csizmadia, *Handbook of Gaussian Basis Sets* Physical Sciences Data, Vol. 24 (Elsevier, Amsterdam, 1985).
[17] M. F. Guest and V. R. Saunders, Mol. Phys. **28**, 819 (1974).
[18] J. B. Rose and V. McKoy, J. Chem. Phys. **55**, 5435 (1971).
[19] B. N. Plakhutin, L. N. Shchegoleva, and G. M. Zhidomirov, J. Struct. Chem., **32**(5), (1991) (in Russian).
[20] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1961).
[21] R. A. Evarestov, Teoret. Eksperim. Khim. **18**, 515 (1982) (in Russian).
[22] I. G. Kaplan, *Symmetry of Many-Electron Systems* (Academic Press, New York, 1975).
[23] G. L. Malli and J. P. Olive, J. Chem. Phys. **43**, 861 (1965).
[24] B. N. Plakhutin, A.V. Arbuznikov, and A. B. Trofimov, to be submitted.
[25] M. Peterson and R. Poirier, MONSTERGAUSS-81, Department of Chemistry, University of Toronto and Memorial University of Newfoundland, St. John's, Newfoundland, Canada.
[26] G.T. Klimko and M. M. Mestechkin, Int. J. Quantum Chem. **37**, 753 (1990).

Received April 10, 1990
Accepted for publication February 19, 1991